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by

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PREPARATION AND CHARACTERIZATION OF GROUP 14 THIOLATES AND EVALUATION OF THEIR POTENTIAL AS PRCURSORS IN THE LOW TEMPERATURE SYNTHESES OF METAL SULFIDES

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PREPARATION AND CHARACTERIZATION OF GROUP 14 ELEMENT *BIS*(THIOLATE) COMPOUNDS AND EVALUATION OF THEIR POTENTIAL AS MOLECULAR PRECURSORS IN THE LOW TEMPERATURE SYNTHESES OF BINARY METAL SULFIDES

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ABSTRACT

Three isomeric lead *bis*(butylthiolate) and tin *bis*(butylthiolate) compounds have been prepared and characterized. Their solid state decomposition, and in the case of the lead *bis*(thiolate) compounds, their thermolyses in suspension in a high boiling hydrocarbon, have been studied. X-ray powder diffraction patterns and scanning electron micrographs of the obtained solid state material are discussed. Volatile co-products of the decomposition have been isolated and characterized.

BACKGROUND

Lead sulfide is employed widely in photoconducting detectors. Lead sulfide-based detectors have a high response in the near-IR and are utilized for applications such as spectrometric sensors, flame monitors and missile guidance systems. Pure crystalline lead sulfide has been prepared previously by the reaction of lead metal with elemental sulfur at high temperatures or by the annealing or subliming of impure or amorphous PbS at 800°C.[1] Atomic layer epitaxy has been employed to obtain PbS thin films at 500°C using H_2S and lead halides or lead β-diketonate compounds as precursors.[2] No mention is found indicating that lead thiolates have been used for the preparation of pure lead sulfide. Although lead thiolates have been known for well over one century,[3] no details on their thermolyses have been published to date. Herein, we report the preparation of three isomeric lead *bis*(butylthiolate) compounds and their decomposition into high purity lead sulfide at temperatures as low as 190°C.

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Tin *bis*(*t*-butylthiolate) has been previously prepared and it has been characterized by single crystal X-ray diffraction.[5] The two isomeric compounds $Sn(Ss\text{-}Bu)_2$ and $Sn(Si\text{-}Bu)_2$ have not been reported to date. We report their preparation and the decomposition of the three isomeric tin *bis*(butylthiolate) compounds by thermolysis. It is noted that comparable reaction chemistry recently has been uncovered for the group 12 elements.[8-10]

RESULTS AND DISCUSSION

Lead *bis*(alkylthiolate) compounds are available readily by the reaction of lead acetate and the appropriate thiol in ethanol (equation 1).[4]

$$Pb(OOCCH_3)_2 \cdot 3\,H_2O \; + \; 2\,R\text{-}SH \xrightarrow[R.T]{EtOH} Pb(SR)_2 \; + \; 2\,HOOCCH_3 \qquad (1)$$

R = *tert*--Butyl, *iso*-Butyl, *secondary*-Butyl

Decomposition was studied first by thermogravimetric analyses. The obtained TGA-plots show a sharp decline in weight starting at about 200°C (Figure 1). The observed weight losses suggest the formation of lead sulfide (Table I). An isothermal TGA experiment was conducted to study the nature of the decomposition (Figure 2). The obtained profile indicates a simple one-step conversion into the binary metal sulfide.

Table I. Thermogravimetric analyses of lead *bis*(butylthiolate) compounds

Compound	Weight Residue	
	Observed	Calculated
$Pb(St\text{-}Bu)_2$	62.11	62.06
$Pb(Si\text{-}Bu)_2$	63.06	62.06
$Pb(Ss\text{-}Bu)_2$	64.21	62.06

Thermolyses then were carried out by heating samples of the prepared lead *bis*(butylthiolate) compounds under vacuum to 250°C. The obtained solid state materials were characterized by elemental analysis, ESCA, XRPD and SEM.[6] High purity crystalline lead sulfide is formed during the thermolysis of $Pb(St\text{-}Bu)_2$. The decompositions of $Pb(Si\text{-}Bu)_2$ and $Pb(Ss\text{-}Bu)_2$ yield slightly impure PbS at the same temperature. The impurities were identified as elemental lead. If the thermolysis is carried out at 400°C, X-ray pure PbS is obtained. Explanations regarding the observations of crystalline impurities are discussed elsewhere.[6-7]

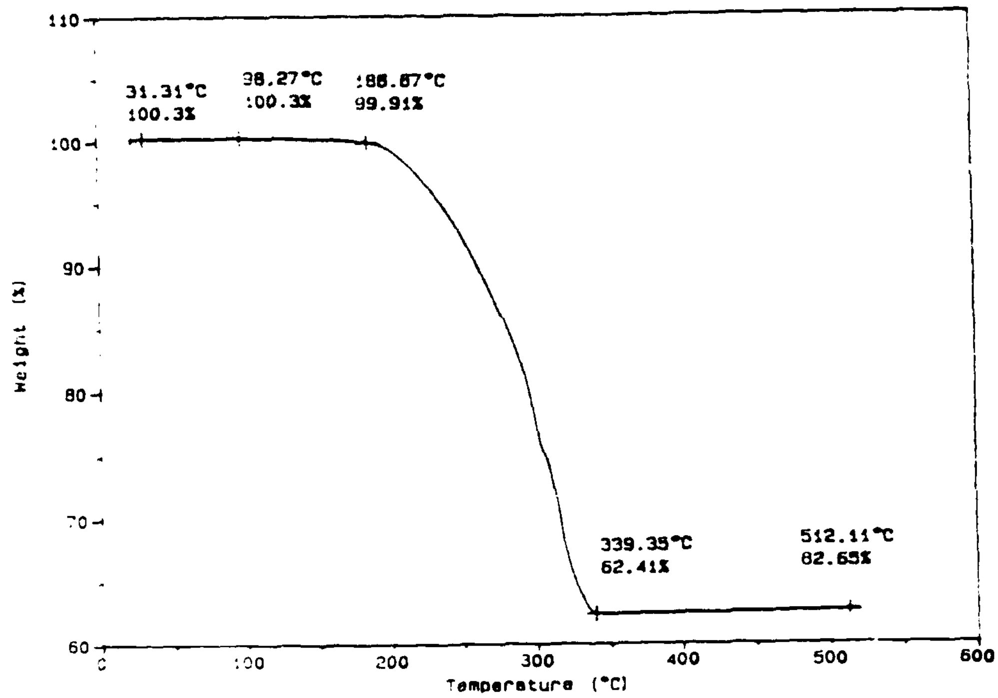


Figure 1. TGA plot of $Pb(StBu)_2$ (N_2 flow, 10°C/min)

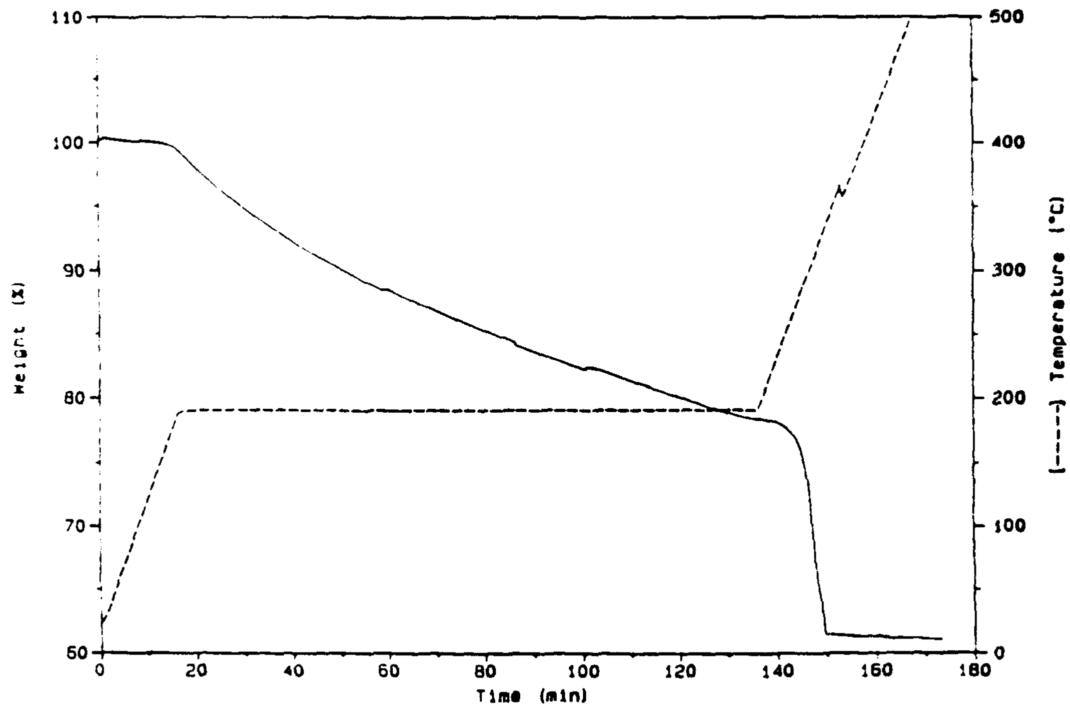


Figure 2. TGA plot of $Pb(StBu)_2$ (isothermal, 180°C, 2h, N_2 flow)

Lead *bis*(*t*-butylthiolate) compounds can be converted into X-ray pure lead sulfide by heating a suspension of the compound in decalin to 190°C for three days. The XRPD pattern of lead sulfide obtained by the decomposition of $Pb(St\text{-}Bu)_2$ is shown in Figure 3 and reveals highly crystalline material. SEM photomicrographs of the obtained PbS indicate the presence of well-formed crystalline material (Figure 4).

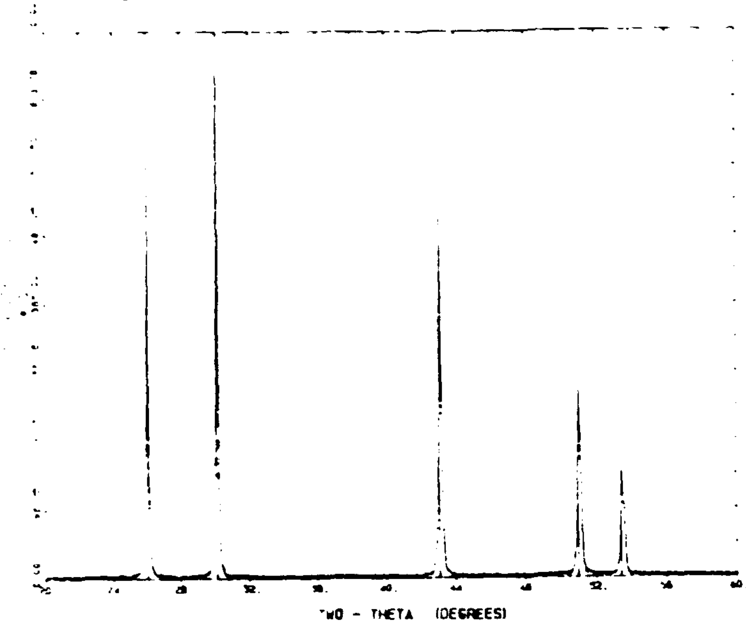


Figure 3. XRPD pattern of PbS obtained by the decomposition of $Pb(StBu)_2$ in decalin (190°C, 3d)

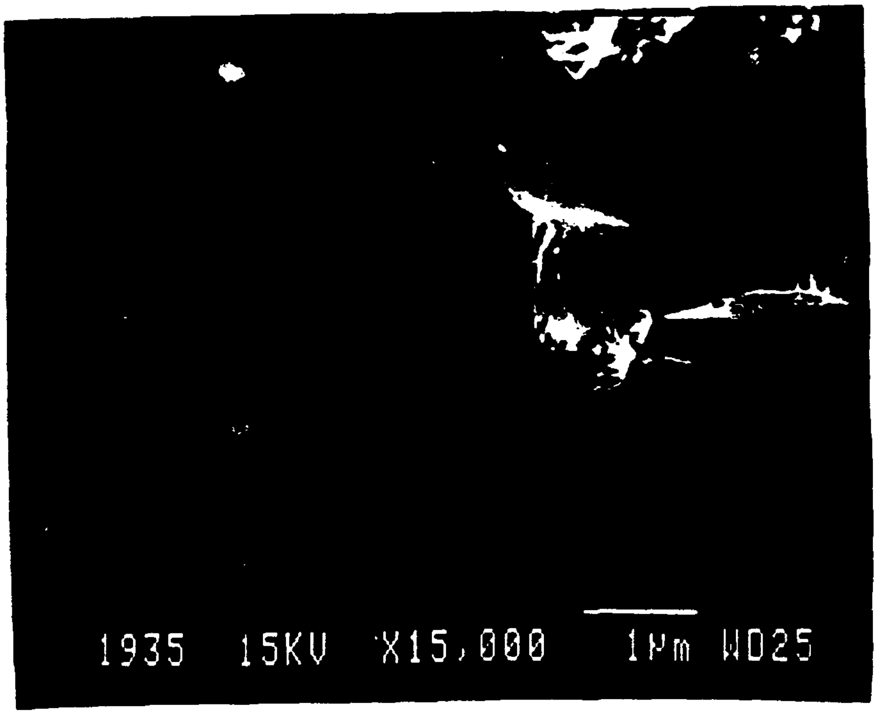


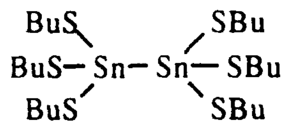
Figure 4. SEM micrograph of PbS obtained by the decomposition of $Pb(StBu)_2$ in decalin

Tin *bis*(butylthiolate) compounds are prepared by the reaction of tin *bis*[*bis*(trimethylsilyl)amide] and the appropriate thiol in THF (equation 2).[5]

$$Sn(N(SiMe_3)_2)_2 + 2\ R\text{-}SH \xrightarrow[R.T.]{THF} Sn(SR)_2 + HN(SiMe_3)_2 \qquad (2)$$

$$R = t\text{-Bu},\ i\text{-Bu},\ s\text{-Bu}$$

The compounds are yellow oils or low melting solids. The solid state decomposition of tin *bis*(butylthiolate) compounds leads to the formation of mixtures of SnS (Herzenbergite) and elemental tin. If the decomposition is stopped prior to completion, a colorless and highly viscous oil is isolated. The compound has the formula $Sn_2(SBu)_6$ (I) as determined by GC/MS.



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SUMMARY

Lead *bis*(butylthiolate) compounds are useful single source precursors for the preparation of lead sulfide. The precursors are readily available and are air-stable. Their decomposition proceeds under mild conditions. Lead *bis*(*t*-butylthiolate) decomposes at temperatures as low as 190°C. Temperatures of 400°C have to be applied to convert the isomeric *i*-butyl and *s*-butyl derivatives into pure lead sulfide. XRPD patterns and SEM micrographs confirm the crystallinity of the obtained lead sulfide. The co-products of the decomposition are volatile and can be removed easily. Tin *bis*(butyl) thiolate compounds are highly air-sensitive oils or low melting solids. They decompose to form a mixture of tin sulfide and elemental tin. Intermediates which are formed when the molecular precursor is converted into a solid state material have been isolated and preliminarily identified.

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